Chemistry 4631

Instrumental Analysis

Lecture 11

UV-Vis Instruments

Types of Instrumentation

- Single beam
- Double beam in space
- Double beam in time
- Multichannel
- Speciality

UV-Vis Instruments

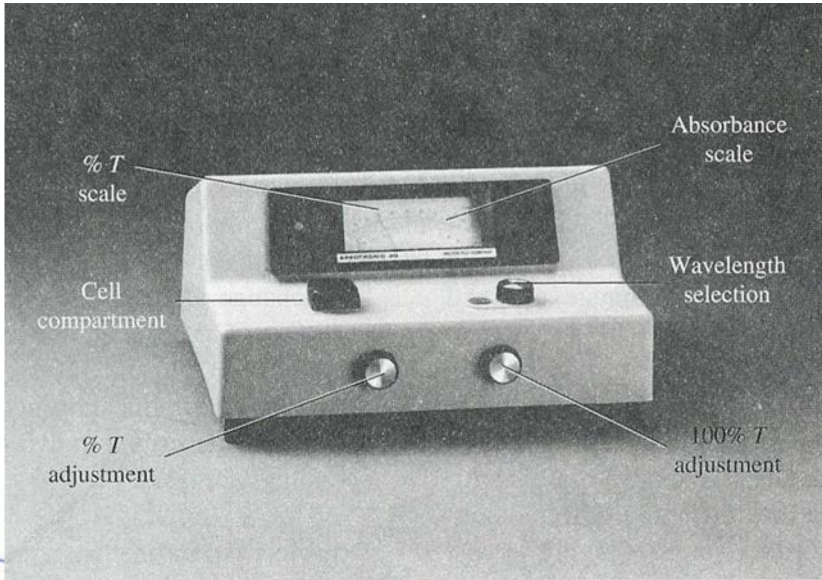
Types of Instrumentation

Single beam

Requires stable voltage supply to keep stable beam intensity.

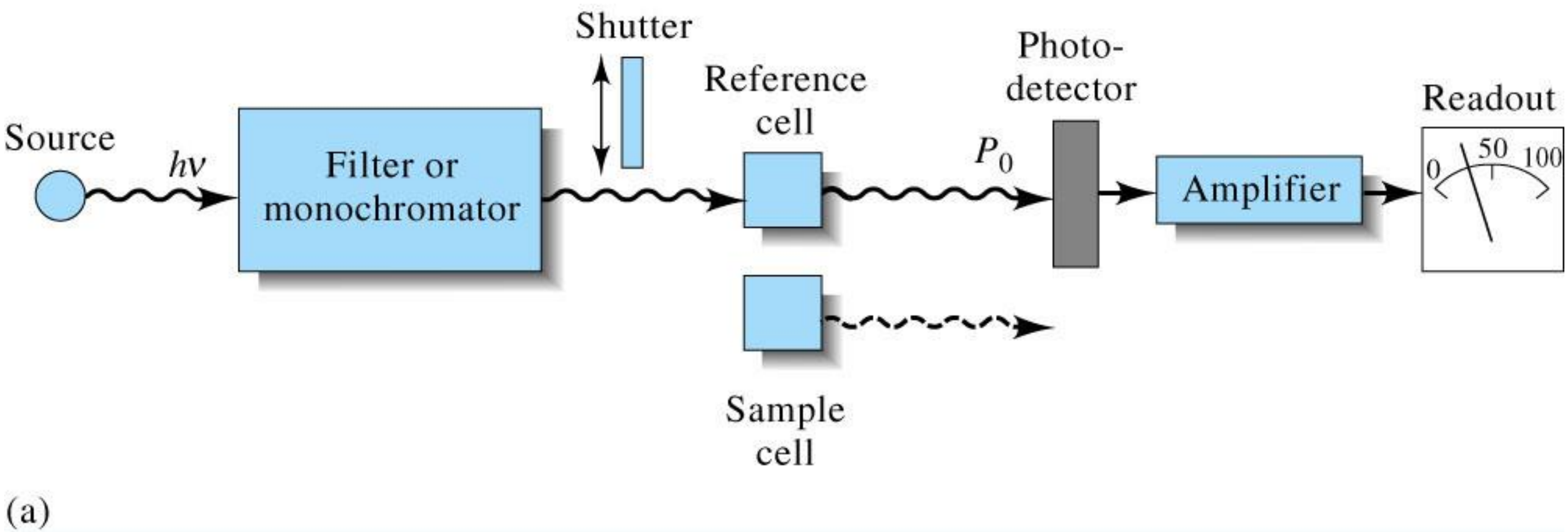
Accuracy generally 1-2%

Example: Spectronic 20



UV-Vis Instruments

Single beam



UV-Vis Instruments

Types of Instrumentation

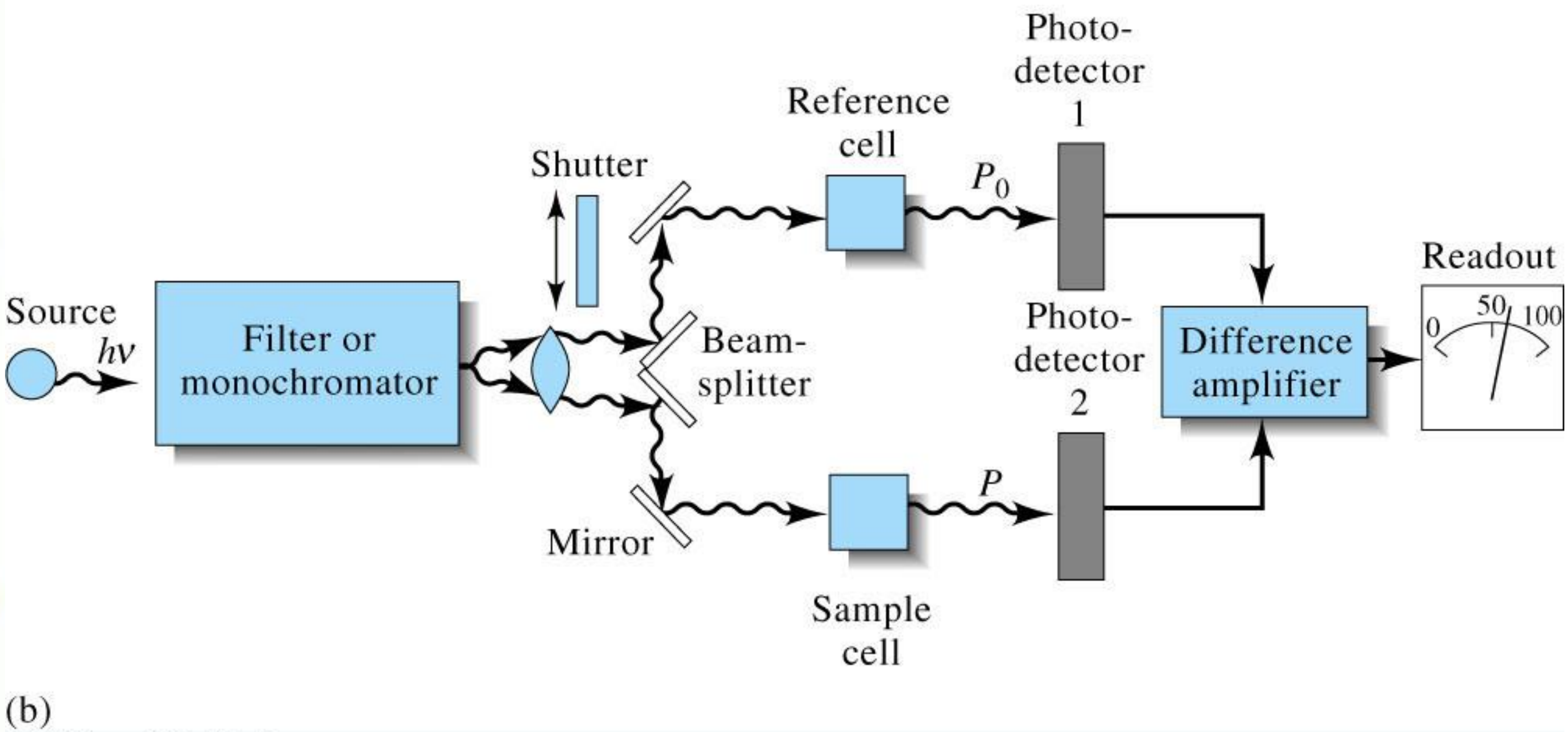
Double Beam

Two beams are formed by V-shaped mirror called a beam splitter.

One beam passes through the reference cell and other through the sample.

UV-Vis Instruments

Double Beam (space)

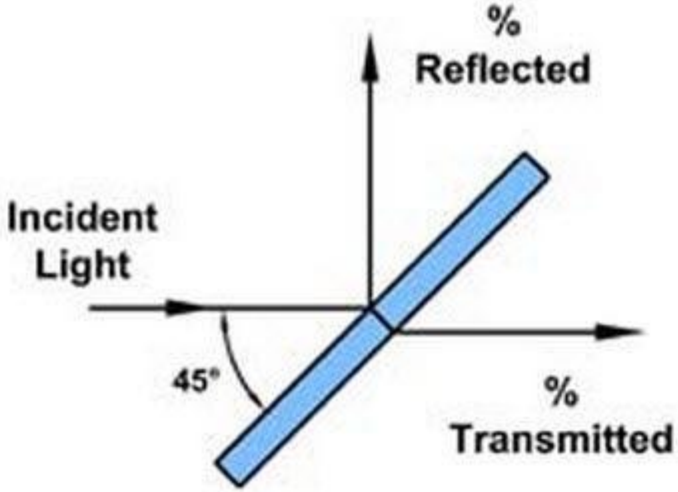


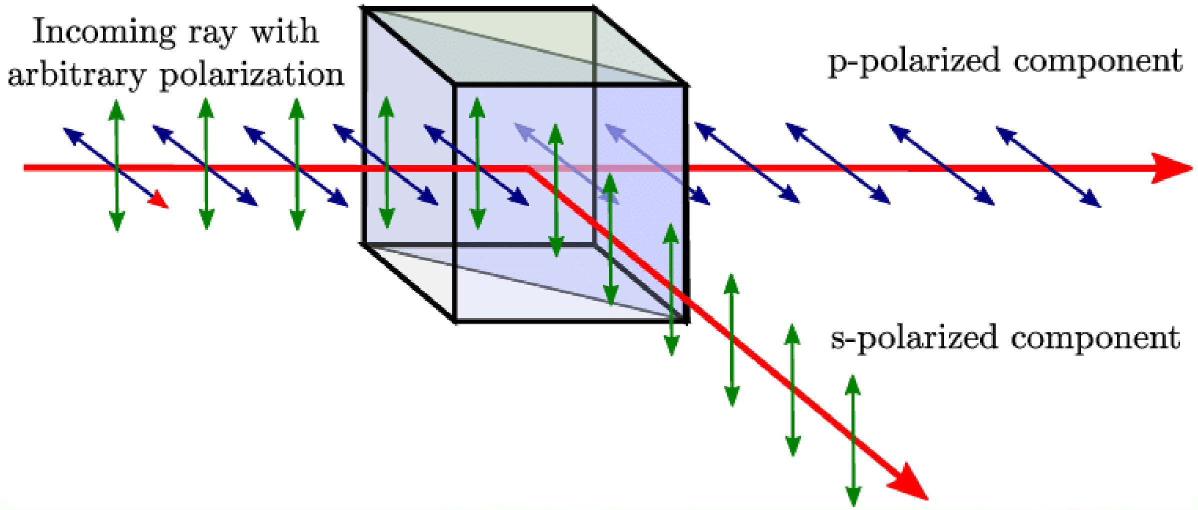
UV-Vis Instruments

Beam Splitter

We saw in making holographic gratings and something similar in design of interference filters.

- 2 triangular prisms
- half-silvered mirror (actually Al)
- dielectric coating





UV-Vis Instruments

Double Beam

Uses an optical null procedure

An optical wedge is added into the reference beam to make the intensity of the reference beam equal to the intensity of the sample beam.

UV-Vis Instruments

Double Beam

Or beam can be separated in time by a rotation sector mirror (chopper) that directs beam either through the reference or sample cell.

The beam is recombined on the other side of the cell and sent to detector.

UV-Vis Instruments

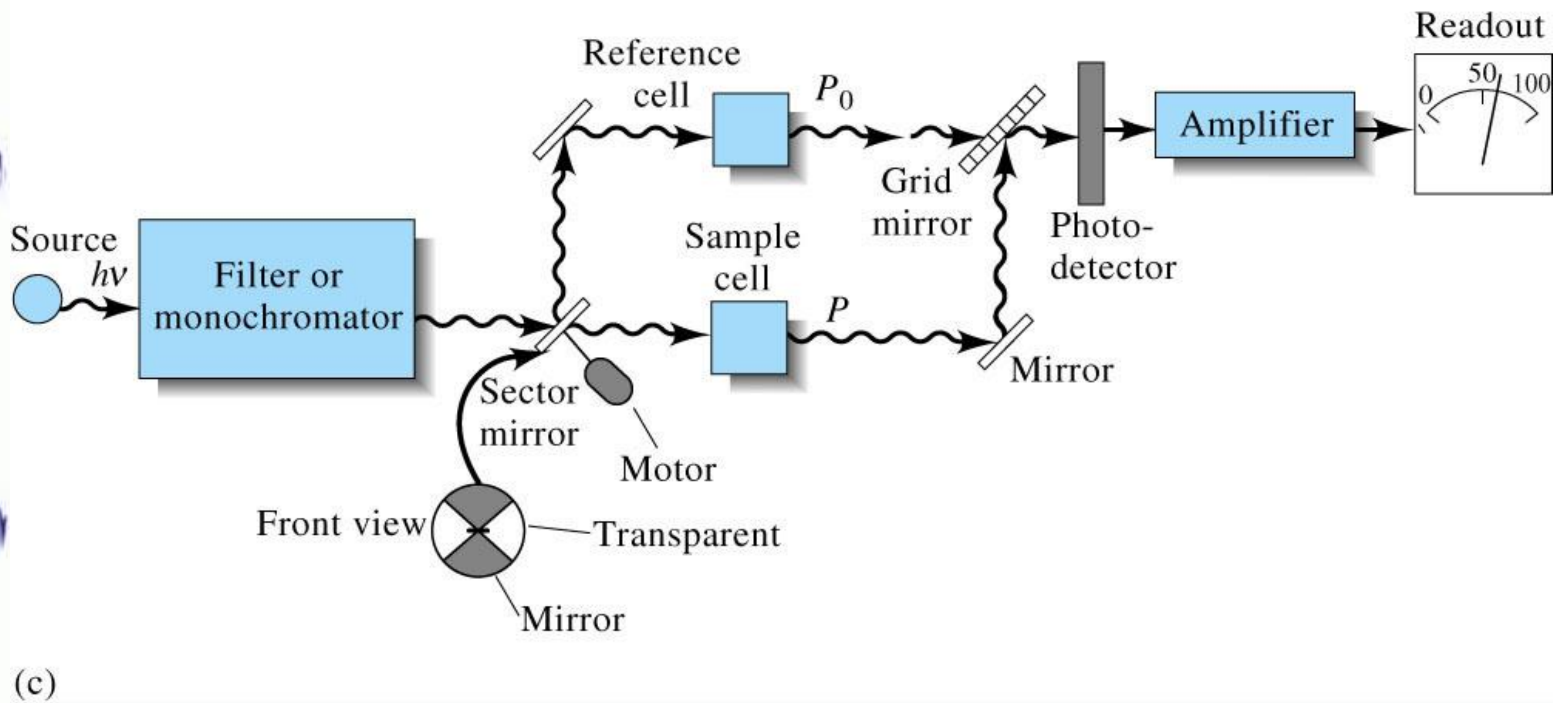
Double Beam

Rotating mirror face is sectioned with half of segments mirrored and half transparent.

The beam through the reference cell is nulled until intensity matches that of the beam coming from the sample cell.

UV-Vis Instruments

Double Beam (time)



Spectrophotometers
Double Beam
for UV/vis

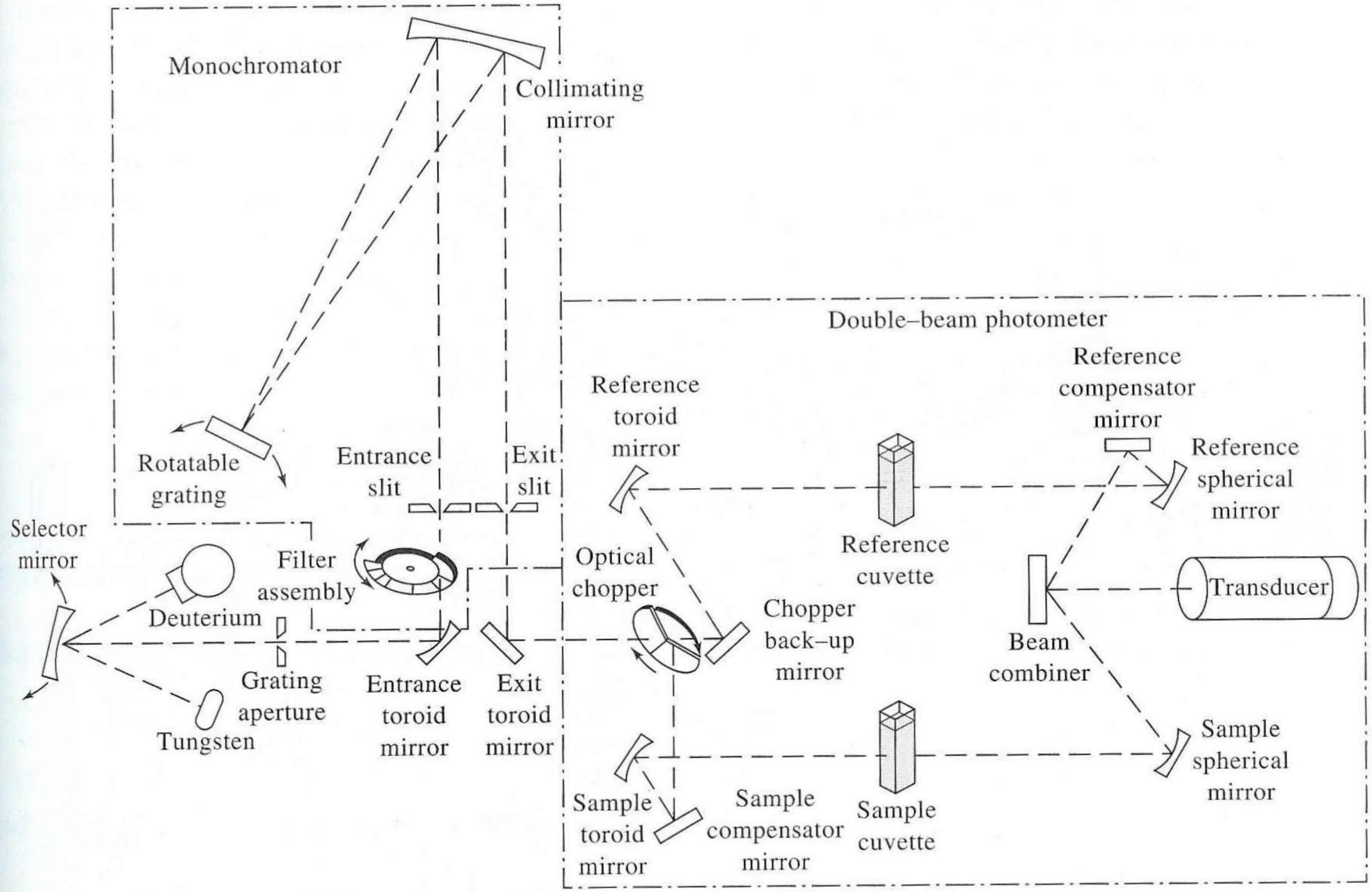
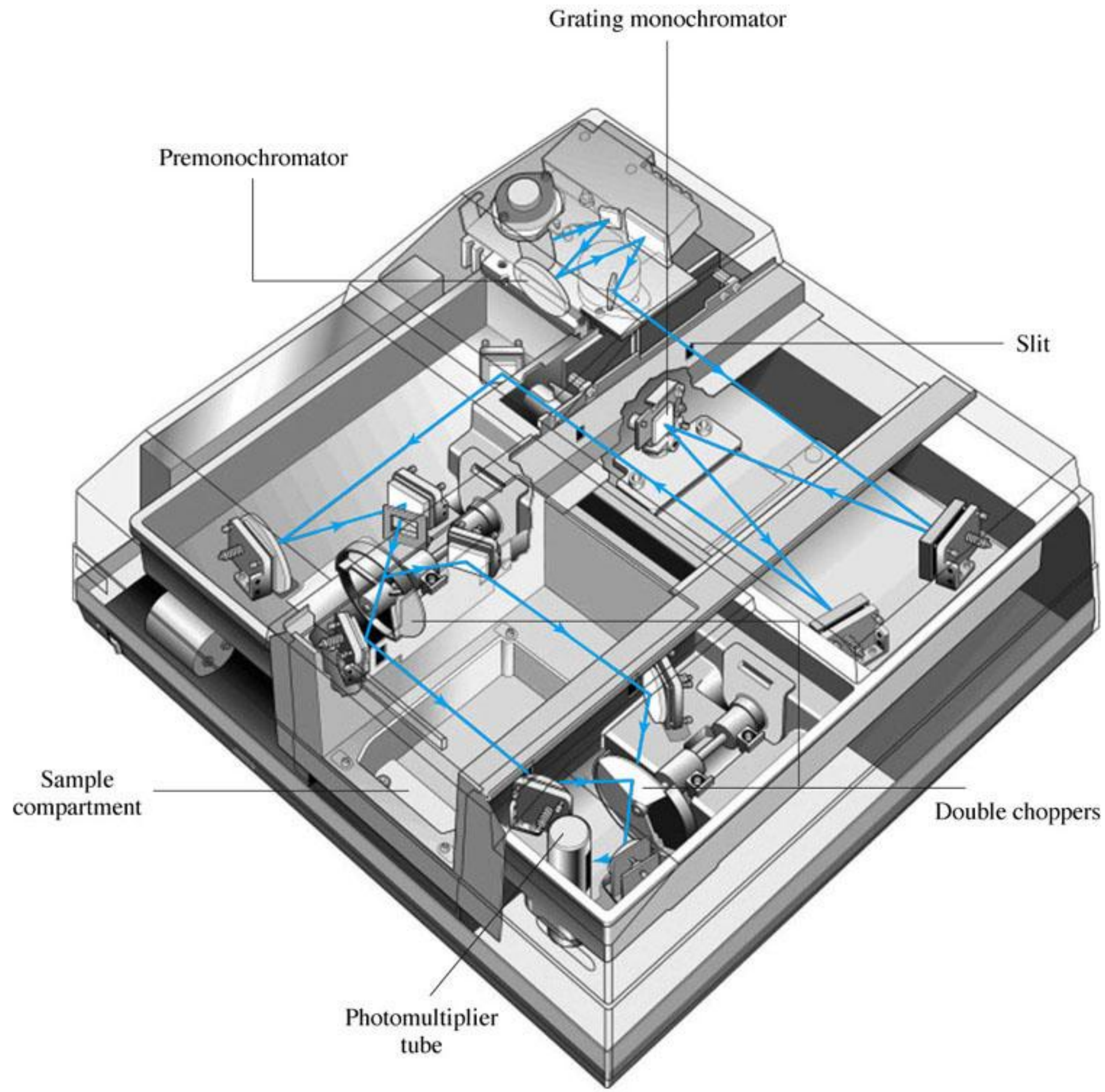


Figure 13-20 A double-beam recording spectrophotometer for the ultraviolet and visible regions; the Perkin-Elmer 57 Series. *(Courtesy of Coleman Instruments Division, Oak Brook, IL.)*

Spectrophotometers
Double Beam
for UV/vis



UV-Vis Instruments

Double Beam

Advantage of double beam:

Compensates for most fluctuations in radiant output of source.

UV-Vis Instruments

Types of Instrumentation

- Single beam
- Double beam in space
- Double beam in time
- Multichannel

UV-Vis Instruments

Types of Instrumentation

- **Multichannel**
  - **Based on array detectors**
  - **Usually single-beam designs**

UV-Vis Instruments

Multichannel

Diode Array Spectrometer

Radiation from the source is focused on the sample and passes to a monochromator with a fixed grating. The dispersed radiation hits a photodiode array transducer.

UV-Vis Instruments

Multichannel

Diode Array Spectrometer

The transducer (chip) consist of a linear array of several hundred photodiodes (256, 512, 1024, 2048).

The chip is 1 – 6 cm in length and individual diode widths are 15 – 50 μm. Each diode has a capacitor and an electronic switch.

UV-Vis Instruments

Multichannel

Diode Array Spectrometer

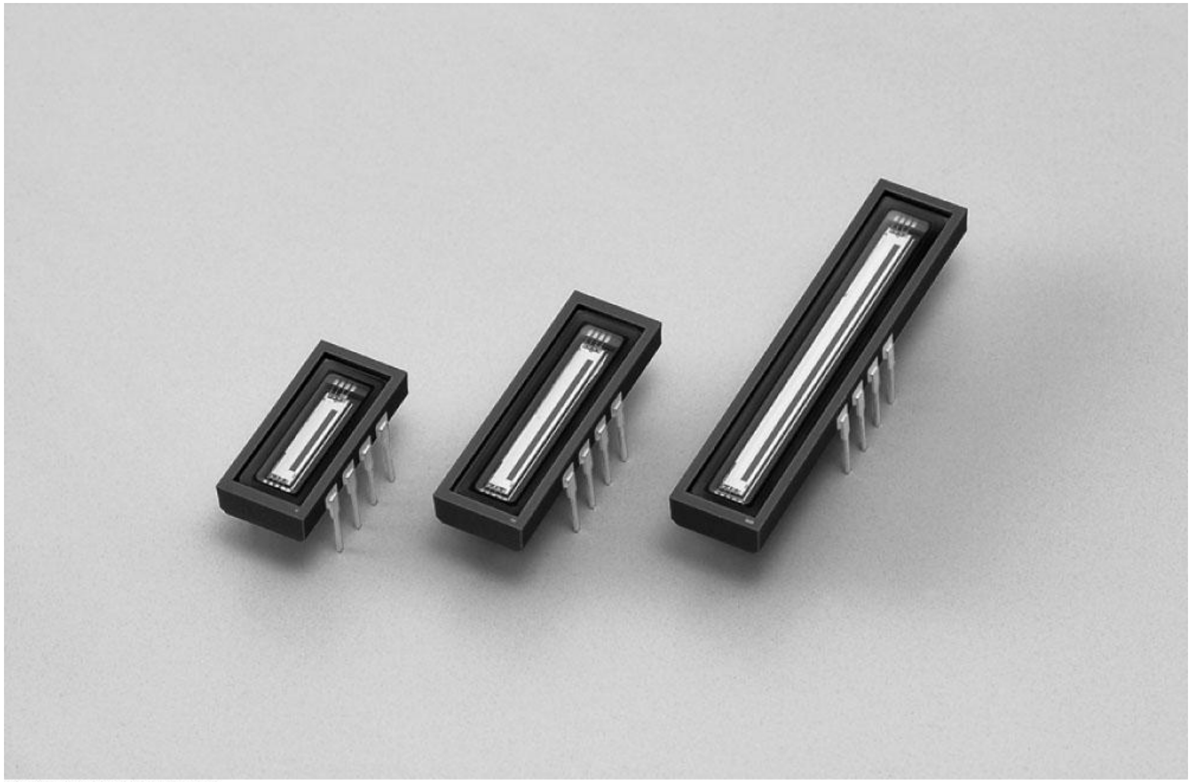
Each capacitor is charged to –5V. Radiation hitting the diode partially discharges the capacitor.

The lost charge is replaced in the next switching cycle.

The entire spectrum can be obtained in one second.

UV-Vis Instruments

Multichannel



Spectrophotometers
Diode Array

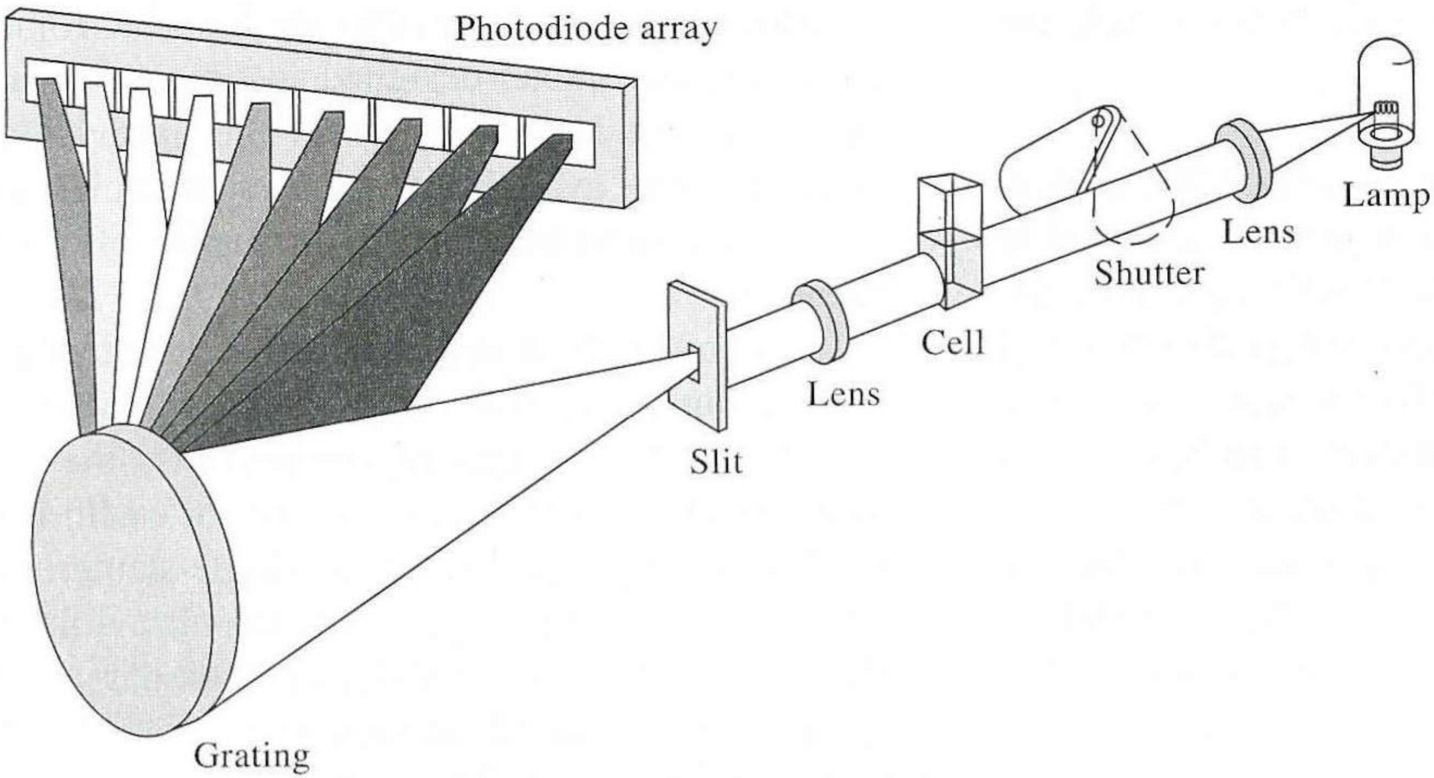


Figure 13-22 A multichannel diode array spectrometer; the HP 8452A. *(Courtesy of Hewlett-Packard Company, Palo Alto, CA.)*

UV-Vis Instruments

Multichannel

Diode Array Spectrometer

Advantages:

- Used for transients intermediate measurements
- Used for kinetic studies
- Can combine with chromatography

Disadvantages:

- Limited resolution (1-2 nm)

UV-Vis Instruments

Double-Dispersion Instrument

- -enhance spectral resolution
- -reduce scattered radiation

2-gratings – 2 monochrometers in series.

Spectrophotometers

Double Dispersing (resolution 0.07 nm)

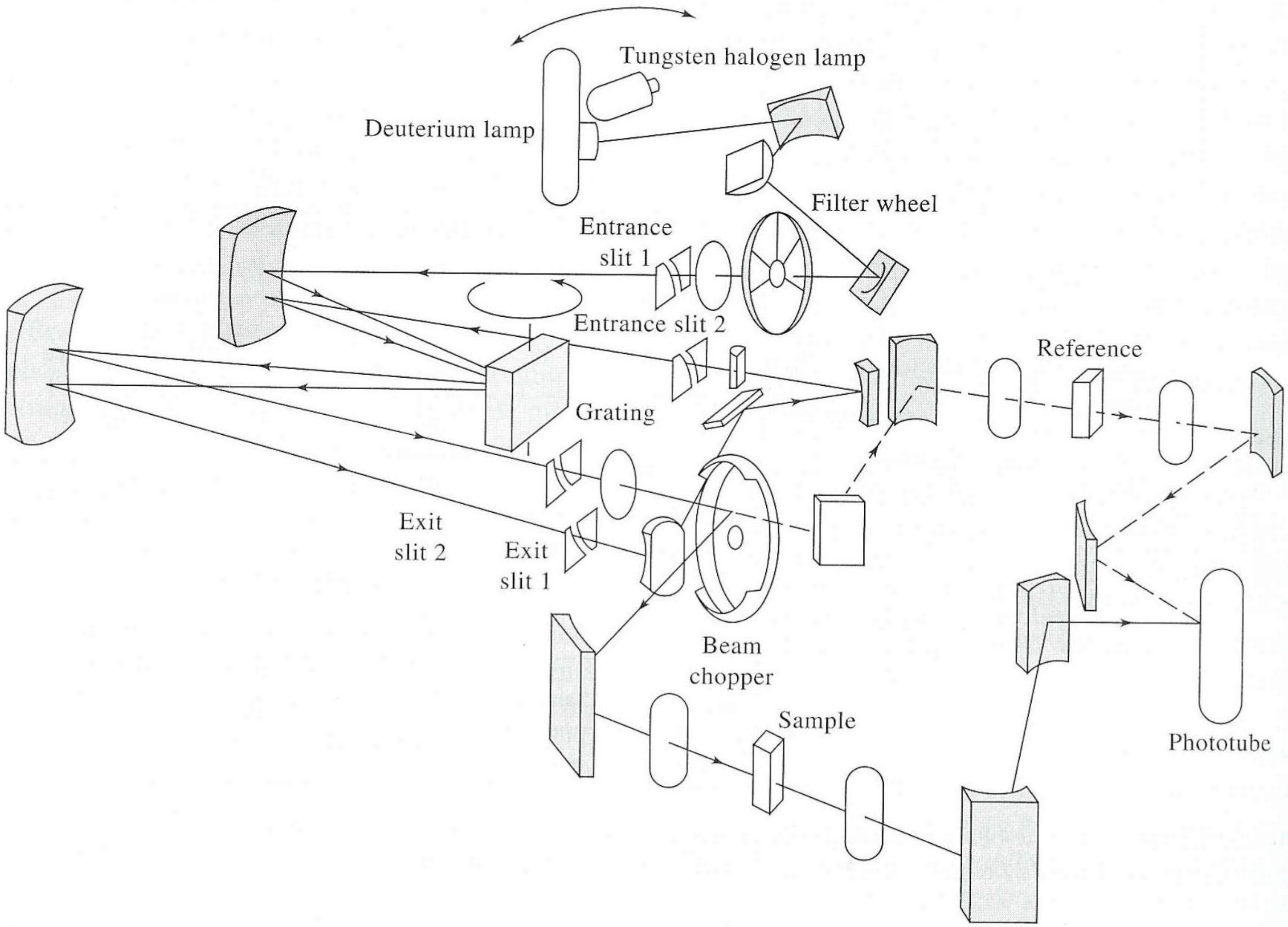


Figure 13-21 A double-dispersing spectrophotometer. *(Courtesy of Varian Instrument Division, Palo Alto, CA.)*

Optical Instruments

Instrumental Noise

Uncertainties in the measurement of transmission and concentration give measurable standard deviations.

Where does this uncertainty in measurement come from?

Optical Instruments

Noise

% error in a signal becomes larger as the signal becomes smaller.

Signal-to-noise (S/N) = mean/std. dev.

General rule S/N > 3 to consider as reliable data

Optical Instruments

Chemical Noise

Typically from changes in variables (not part of the measured data) during the experiment,

i.e. changes in pressure, T, humidity; vibrations; outside light or electronic signals (environmental); changes in atmosphere; etc…

Optical Instruments

Environmental Noise

Components in the instrument can act like an antenna to pick up electromagnetic energy in the environment and convert it to an electrical signal.

Optical Instruments

Environmental Noise

Can reduce by shielding, grounding, or destructive interference.

Optical Instruments

Instrumental Noise

Electrical or mechanical noise associated with a component in the instrument.

Sources:

- $s_T = k_1$
- $s_T = k_2 (T^2 + T)^{½}$
- $s_T = k_3 T$

(s_T – standard deviation of transmittance measurement)

Optical Instruments

Instrumental Noise

Thermal or Johnson noise

$$s_T = k_1$$

Encountered with less expensive equipment and readouts with limited resolution.

Random noise.

Optical Instruments

Instrumental Noise

$$s_T = k_1$$

Also for IR equipment, due to Johnson noise (thermal noise) in the detector.

Johnson noise is caused by thermal agitation of electrons or carriers in resistors, capacitors, transducers, etc.. This creates voltage fluctuations.

Optical Instruments

Instrumental Noise

$$s_T = k_1$$

How to minimize?

-keep instrument cool

-reduce frequency or response time in circuits, i.e. the slower the response to a signal, the lower the thermal noise

Optical Instruments

Instrumental Noise

$$s_T = k_2 (T^2 + T)^{1/2}$$

Limits precision of high quality instruments.

Due to shot noise (random noise)

Optical Instruments

Instrumental Noise

$$s_T = k_2 (T^2 + T)^{1/2}$$

Shot noise

When electrons or charge particles cross a junction such as at pn interfaces or movement of electrons from a cathode to an anode in a PMT.

Can minimize by slowing the response of the circuit.

Optical Instruments

Instrumental Noise

$$s_T = k_3 T$$

From a slow drift in radiant output of the source called source flicker noise (or 1/f noise).

Optical Instruments

Instrumental Noise

$$s_T = k_3 T$$

Flicker noise is inversely proportional to the frequency of the signal.

Becomes significant at frequencies below 100 Hz.

Shows up as long-term drift.

Minimized by good voltage power supplies or a split beam arrangement.

Optical Instruments

TABLE 13-3 Types and Sources of Uncertainties in Transmittance Measurements

Category	Characterized by[a]	Typical Sources	Likely To Be Important In
Case I	$s_T = k_1$	Limited readout resolution	Inexpensive photometers and spectrophotometers having small meters or digital displays
		Heat detector Johnson noise	IR and near-IR spectrophotometers and photometers
		Dark current and amplifier noise	Regions where source intensity and detector sensitivity are low
Case II	$s_T = k_2\sqrt{T^2 + T}$	Photon detector shot noise	High-quality UV-visible spectrophotometers
Case III	$s_T = k_3 T$	Cell positioning uncertainties	High-quality UV-visible and IR spectrophotometers
		Source flicker	Inexpensive photometers and spectrophotometers

Assignment

- See book and manufacturer websites for more instrument diagrams
- See Class Notes (Extra) – at class website